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Evaluation of Cryogenic Trapping as a Means for Collecting Organic Compounds in Ambient Air

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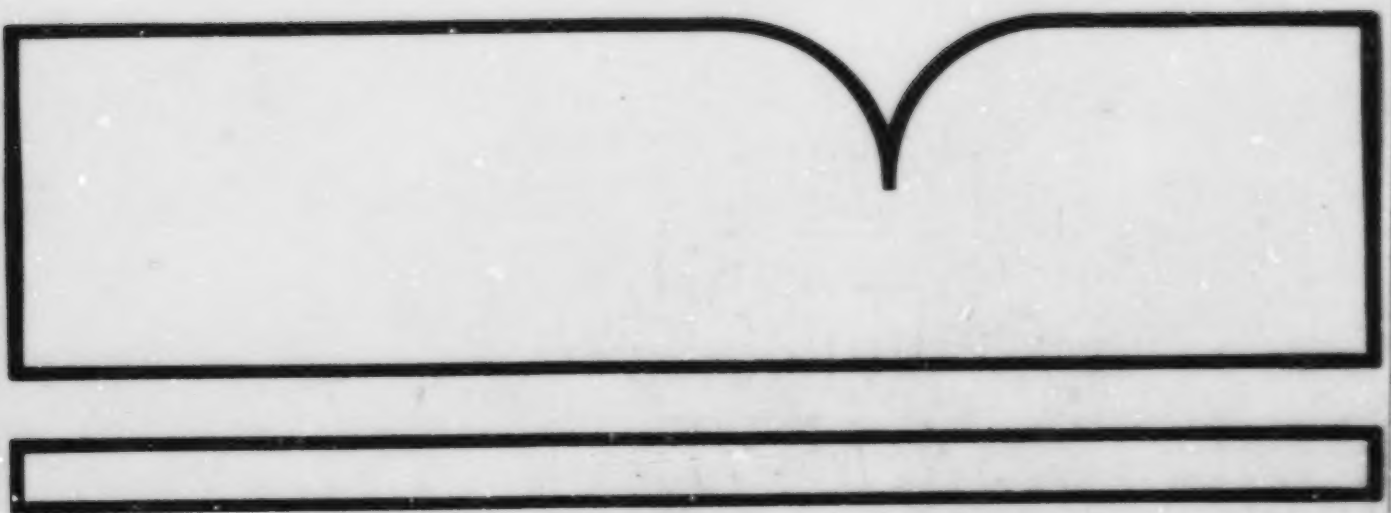

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EVALUATION OF CRYOGENIC TRAPPING AS A MEANS FOR COLLECTING ORGANIC COMPOUNDS IN AMBIENT AIR

by

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16. ABSTRACT

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Collection and recovery efficiencies from the trap (1 to 10 ppbv compound) were 100 ± 5 percent with this preconcentration technique. The integrity of sample components was unaffected by co-collection of ozone and nitrogen dioxide at typical ambient concentrations. Two nominally identical automated gas chromatographic instruments gave nearly identical results during simultaneous monitoring of calibration mixtures and laboratory air. Calibration mixtures at ppbv levels were also collected in passivated stainless steel canisters. Statistical analysis of the data indicated that the canisters would serve as acceptable storage vessels for most of the volatile organic compounds tested.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsbility for: assessment of environmental monitoring technology and systems for air; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

New monitoring procedures for volatile organics in ambient air have recently evolved using modern capillary column gas chromatography. The high resolution capability combined with sample preconcentration procedures and gas chromatographic detectors responding to specific subgroups of volatile organics has significantly advanced our monitoring capabilities. This study addresses the design and characterization of an automated monitoring system. Emphasis is placed on the evaluation of system features that can affect the sample integrity during reduced temperature preconcentration.

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ABSTRACT

The methodology used in reduced temperature preconcentration of volatile organic compounds has been tested using a prototype automated gas chromatographic system. Mixtures of sixteen volatile organic compounds in humidified zero air were passed through a Nafion tube dryer and the organic compounds were collected on a reduced-temperature trap. The dryer reduced the water concentration without significantly affecting the integrity of the trace organic species. The selective reduction of water vapor improves the chromatography of the trace organics and likewise permits processing larger sample volumes.

Collection and recovery efficiencies from the trap (.3 to 3 ppbv compound) were 100 $\pm$ 5 percent with this preconcentration technique. The integrity of sample components was unaffected by co-collection of ozone and nitrogen dioxide at typical ambient concentrations. Two nominally identical automated gas chromatographic instruments gave nearly identical results during simultaneous monitoring of calibration mixtures and laboratory air. Calibration mixtures at ppbv levels were also collected in passivated stainless steel canisters. Statistical analysis of the data indicated that the canisters would serve as acceptable storage vessels for most of the volatile organic compounds tested.

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SECTION 1

INTRODUCTION

The atmosphere contains a complex mixture of organic compounds. Many of these emitted chemicals have been found to be highly toxic substances. Data on the identity and concentration levels of these compounds in urban and rural environments are continually being gathered by researchers who are attempting to better understand the chemistry and fate of these chemicals as well as the extent of human exposure to these compounds(1-5). From an analytical standpoint, this data gathering task has been formidable. However, these efforts have been dramatically improved in recent years through the use of capillary column gas chromatography coupled to compound-specific detection systems. Furthermore, the interfacing of the gas chromatograph to a mass spectrometer detector has permitted positive identification of many of these atmospheric constituents(6-9).

Most of these toxic chemicals are present at ppb levels or less and preconcentration is often necessary for accurate chemical analysis. Presently the two primary ambient air preconcentration techniques employed in delineating atmospheric organic burdens are cryogenic trapping and solid adsorbents.

Cryogenic trapping can involve either of two collection procedures. With the first procedure, whole air samples are entirely condensed within suitable collection devices by cryogens such as liquid nitrogen or liquid helium. Both cryogens are sufficiently cool to serve as the cryogenic pump in this collection process. This approach is normally used in studies where remote sampling is being conducted(10-12). Once the sample is collected, the coolant is removed and the container returned to the laboratory for subsequent analysis.

The other cryogenic trapping procedure involves passing air through a reduced-temperature trap. At the appropriate temperature, trace organic species will condense onto the trap surfaces while oxygen and nitrogen pass through the system. Reduced-temperature trapping has several limitations which must be considered when designing a sampling and analytical system. A limiting factor of major importance is the co-collection of water in the sampling trap. One liter of air at 50 percent relative humidity and 25 C will contain approximately 10 mg of water, which appears as ice in the collection trap. The possibility of the ice plugging the trap and stopping sample flow is of concern, and water transferred to the gas chromatographic capillary column may also cause plugging and deleterious column effects. Furthermore, during sample preconcentration, chemical reactions may also occur in the collection trap. Possible reactants could include ammonia/acids, ozone/olefins, etc.

The Advanced Analysis Techniques Branch of the Environmental Monitoring Systems Laboratory (EMSL) is responsible for the development and evaluation of state-of-the-art and emerging analytical techniques for the determination of organic compounds in ambient air. Recently a priority listing of volatile organics has been established and the EMSL is focusing on further development of analytical methodology associated with the detection of these compounds. Primary emphasis has been placed on developing field-compatible analytical systems.

Recently a prototype automated analytical system incorporating cryogenic trapping for sample preconcentration has been developed jointly by EPA and the Battelle laboratory. System hardware utilizes capillary column gas chromatographic separation techniques along with flame ionization and electron capture detection. Software development using the basic programming capability of the gas chromatography system permits calibration and ambient sampling to be achieved with minimal operator interfacing. In this report, we shall describe instrumentation hardware and software and shall discuss laboratory experiments designed to test the suitability of the prototype system for preconcentration of volatile organic compounds (VOCs) in ambient air. The VOCs selected were propane, vinyl chloride, vinylidene chloride, trichlorotrifluoroethane, chloroform, 1,2-dichloroethane, methyl chloroform, benzene, carbon tetrachloride, trichloroethylene, 1,3-dichloropropene(cis), 1,3-dichloropropene(trans), toluene, 1,2-dibromoethane, tetrachloroethylene, chlorobenzene, o-xylene, benzyl chloride, and hexachlorobutadiene.

The following laboratory experiments were carried out:

(1) A Perma-Pure dryer was tested to determine if water vapor could be selectively removed from the gas stream also containing the 16 target compounds without affecting the integrity of the organics in the gas phase.

(2) Collection and recovery efficiencies of the organic compounds were determined.

(3) Studies were also conducted with the target compounds to examine potential interference or artifact effects from co-collected ozone and nitrogen dioxide gases.

(4) A prototype calibration device was interfaced to the overall system and tested. Software was developed to permit automatic operation and calibration of the gas chromatography (GC) system.

(5) Side-by-side comparison of two prototype automated sampling and analysis units was carried out at the EPA facility. Calibration mixtures and ambient air samples were analyzed.

(6) In a joint effort with EPA, a comparison was made between analytical results for samples collected and temporarily stored in small metal cylinders, with data collected during real-time sampling.

SECTION 2

CONCLUSIONS

An automated sampling and gas chromatographic analysis system employing reduced temperature preconcentration methodology has been tested in the laboratory. During the laboratory experiments, two Nafion tube dryers were evaluated and found to reduce water vapor selectively in the gas phase without affecting the integrity of trace organic species also present. The selective reduction of water vapor improves the chromatographic resolution of the trace organics and likewise permits larger sample volumes to be processed. Experiments showed that collection and recovery efficiencies of sixteen volatile organic compounds at low ppbv levels (.3 to 3) were 100 ± 5 percent with this preconcentration technique. Ozone and nitrogen dioxide interference studies indicated that none of the target compounds was affected by the additional presence of these reactive species. Furthermore, no artifact peaks or deleterious column effects were observed during or after these tests.

In a cooperative effort with EPA, two nominally identical automated GC systems were intercompared with samples, both calibration mixtures and ambient air, drawn from a common manifold. Statistical analysis of the calibration data involved regressing concentration on raw area and determining the least squares regression line. A percent relative error of less than ten was obtained for fourteen of the sixteen compounds listed in Table 7 when comparing the estimated concentration to the actual concentration. The remaining two compounds, benzyl chloride and hexachlorobutadiene, exhibited relative error values of ∿20 percent at the lowest non-zero concentration level (4 ppbv). Simultaneous sampling of laboratory air from a common manifold resulted in reasonable agreement between the two instruments. Nine target compounds were identified and quantified. The results indicated an overall precision of ±10 percent.

In EPA conducted experiments, sixteen target compounds (see Table 11) were stored at low ppb concentrations (2-5 ppbv) in passivated stainless steel containers and examined over a seven day period. Statistical treatment of the data indicated that after four days of storage, measured concentrations for all sixteen compounds were within ±8 percent of the initial values. After seven days the average benzyl chloride concentration decreased by ∿19 percent while hexachlorobutadiene increased by ∿11 percent.

During the program, software was developed to facilitate the monitoring and calibration needs of the automated GC sampling and analysis system. In addition to controlling zone heating and cooling, sample collection and injection, chromatographic run conditions and data processing, the software provided single point or multipoint calibration subroutines to be nested into the overall sampling and analysis strategy.

SECTION 3

RECOMMENDATIONS

A gas chromatographic system employing reduced temperature preconcentration for the collection of VOC's has been tested with respect to sample drying procedures, co-collection of reactive ambient air species, and collection and release efficiency. An automated GC system has been used to facilitate the laboratory tests.

The following recommendations are suggested:

- The automated GC system should be field tested. The two automated systems should be evaluated side-by-side during the first phase of the field program. Subsequently, the sample collection cycle would be offset so as to permit complete time coverage with both instruments. The cryogenic sampling system should also be compared with other preconcentration techniques such as solid adsorbents (Tenax, Carbosieve) and passive dosimeters. These tests would provide much needed information regarding the advantages and disadvantages of each technque.

- Many of the target compounds tested in this study will co-elute with other ambient air species. Although the combination of capillary column, and flame ionization and electron capture detectors used in the current program help alleviate some of these concerns, other more selective detectors are needed. Integrating a mass-selective detector into the automated gas chromatographic system is recommended. The mass-selective detector offers both total ion and selected ion monitoring capability and will thus provide both qualitative and quantitative information. The increased specificity of this detector over other detection systems will allow better differentiation of co-eluting GC peaks and thus improve present quantitative capability.

SECTION 4

EXPERIMENTAL

CHEMICALS

For the basic laboratory studies, target compounds were obtained from the Eastman Kodak Company and the Baker Chemical Company. Compounds were ~98 percent pure (dichloropropene was 95 percent pure). Liquid standards were made by diluting the neat reagents with methanol. Compound response factors were determined by injecting diluted liquid standards and comparing peak areas to benzene standards. Gas mixtures were prepared by injecting predetermined amounts of each test compound into a cylinder that had been partially evacuated to insure total vaporization of the standard. Once the mixture had equilibrated, the cylinder was pressurized to 1200 psig with "hydrocarbon free" air. The gas mixtures were analyzed by GC-flame ionization detection techniques and compared on the basis of ppb carbon response to an NBS propane standard.

During the latter phase of the program two pressurized cylinders from Scott Environmental Technology, Inc. were acquired. These gas mixtures contained the target compounds at nominal concentrations of 10 ppmv in nitrogen. These mixtures were utilized in conjunction with the prototype calibrator during intercomparison of two automated GC systems and during the canister analysis study.

INSTRUMENTATION

The automated GC system used for sampling and analysis was composed of two instruments as shown in Figure 1. Sample collection was accomplished with a modified Nutech model 320-01 cryogenic unit. The Nutech instrument contained two subsystems. An electronics console was employed for setting and controlling various temperature zones, while the sample handling unit contained the six-port valve and cryogenic trapping components. Three temperature zones were controlled by the console and included the valve, trap, and transfer lines. The valve and transfer lines were maintained at 120 C. During sample collection the trap temperature was regulated by the electronics console, which controlled the release of liquid nitrogen via a solenoid valve. For the current study the temperature setpoint of the trap during sample collection was -160 C $\pm$ 5 C. A cylindrical 250-W heater was used to heat the trap during the sample desorption cycle. Direct thermal contact between the heater and trap provided rapid heating (-160 C to 120 C in 60 sec) and efficient transfer of the sample components onto the gas chromatographic column. The sample trap was constructed of 20-cm by 0.2-cm i.d. stainless steel tubing packed with silanized glass beads (60/80 mesh). A Seiscor six-port air-actuated valve (Seismograph Service Corp., Tulsa, Oklahoma) was used

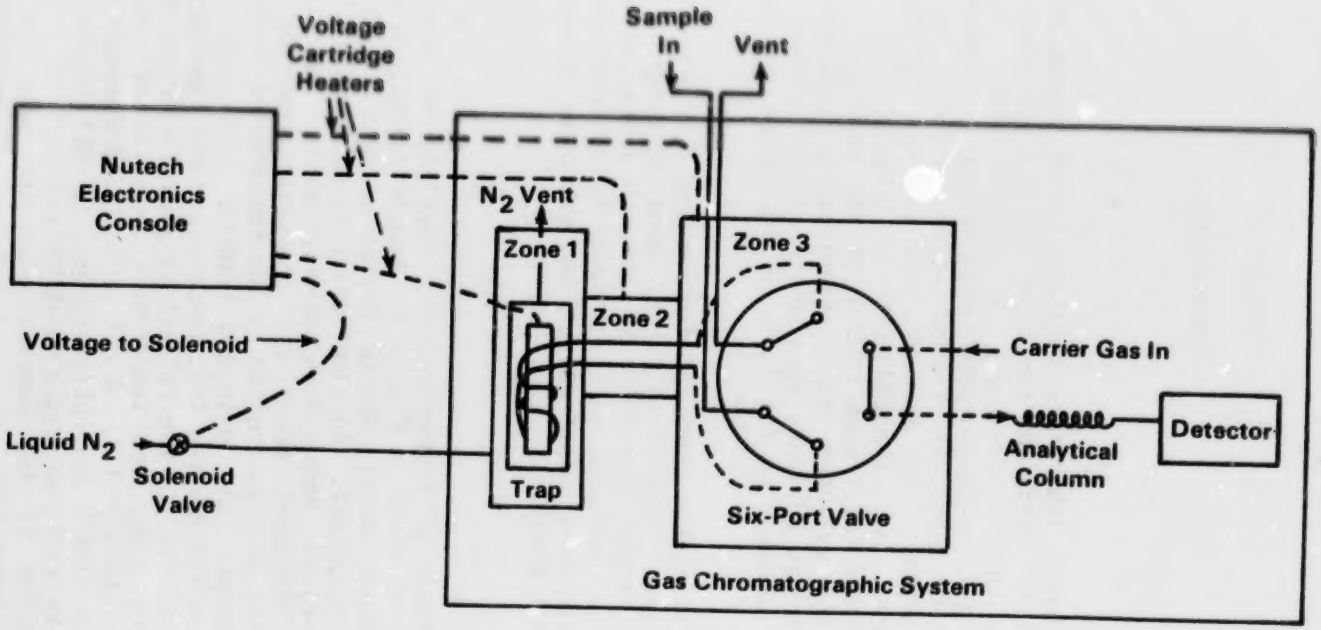

Figure 1. Diagram of automated sampling and analysis system.

to facilitate sample collection and injection. Figure 1 shows the GC valve configured for collection of VOC's (i.e., sample air is diverted through the trap and out the vent port). Switching the valve directs carrier gas through the trap and into the analytical column.

Sample analysis was achieved with a Hewlett-Packard model 5880A (Level 4) gas chromatograph equipped with flame ionization and electron capture detectors. A 50-m by 0.32-mm i.d., OV-1 fused silica column (Hewlett-Packard) was used to resolve the target compounds. The column flow was maintained at a linear velocity of 30 cm/sec (flow controlled system). Zero grade helium (Matheson) served as the carrier gas, and zero grade nitrogen (Matheson) was used as the make-up gas to provide proper electron capture operation. Optimum analytical results were achieved by temperature programming the gas chromatographic column from -50 C to 150 C at 8°/min. During the initial laboratory tests the effluent from the GC column was directed either to the flame ionization or the electron capture detector. During the latter phase of the program a tee was constructed (low dead-volume union with a two-hole ferrule) and the column exit flow was split to both detectors. The canister sampling and GC intercomparison studies were completed with the column in this configuration. A more detailed description of the overall automated system is reported elsewhere.(13)

A gas-phase dynamic dilution system from Columbia Scientific Industries was employed to generate ppb and ppt mixtures of the target compounds during the basic laboratory studies. This unit was also used to produce various concentrations of ozone and nitrogen dioxide. Zero air from an Aadco, Inc. clean-air generator was employed for sample dilution. Internal mass flow controllers provided accurate gas flows, which were verified with a soap-film bubble meter. An EG&G model 911 hygrometer provided data on relative humidity. A sling psychrometer provided a calibration check of the hygrometer.

A Perma Pure dryer (model MD-125F) with a tubular hygroscopic ion-exchange membrane (Nafion) was used to remove water vapor selectively from mixed gas streams. The dryer was purchased in a shell and tube configuration. The tube size was 30 cm by 0.1 cm i.d. and was imbedded within a shell of Teflon tubing with 0.25 cm i.d. Sample flow through the tube was maintained at 60 mL/min. A countercurrent flow of dry zero air (200 mL/min) was used to purge the shell. Literature data on the drying performance of this unit under our experimental conditions show a product dew point of less than -5 C when the incoming wet stream has a dew point of 24 C.(14) Experiments to verify these data were not conducted.

In order to implement automatic calibration in the sampling and analysis system, a prototype calibrator was provided by EPA. Following receipt of the unit several modifications were made to better implement the calibration procedure. The following is a brief description of the instrument. More detailed information is reported elsewhere.(15)

The equipment permits a single stage dilution of a calibration gas mix with a compressed "zero" gas. Two flow controllers (Tylan Corp., Carson, California) are used to achieve dilution ratios near 1000:1. The zero gas

flow is manually preset; the calibration gas flow rate is controlled from the HP 5880 microprocessor by selecting one of four possible "fixed" voltages for its flow controller. Each control voltage is supplied via a reed relay that is closed by the execution of a keyboard command. Figure 2 shows a diagram of the flow scheme in the single stage dilution mode of operation. Solenoid valves 9, 11 and 12 are used for other modes of calibration but are depicted to illustrate the actual valve positions. The vent line downstream of the glass mixing chamber prohibits accidental over-pressurization of the apparatus during ambient air sampling.

PROCEDURE

Perma Pure Dryer

The experimental apparatus shown in Figure 3 was designed to determine the effects of the Perma Pure dryer upon the integrity of the target compounds. An impinger was used to humidify the sample. Mixtures Nos. 1 and 2 contained the 15 target compounds listed in Table 3 in concentrations ranging from 20 to 250 ppb. A CSI dilution system was used to generate ppt concentrations for those compounds responding to the electron capture detector. When tests were conducted on those compounds responding to the flame ionization detector, the dilution system was bypassed and the sample was fed directly to the impinger unit. This modification was necessary to deliver sufficient material to the flame ionization detector. A five mL sample loop was employed for these tests, with constant flow maintained by an orifice/rotameter/pump assembly. Several experiments were performed under dry conditions (i.e., no water added to the impinger). Subsequent runs were carried out after the impinger was filled with distilled water. The outlet relative humidity was measured at the vent position with the hygrometer.

Collection and Recovery Efficiencies

Cryogenic collection and recovery efficiency studies of the target compounds were carried out by replacing the five mL sample loop with the freeze-out trap. An apparatus to measure sample volume was used in place of the orifice/pump assembly to determine more accurately the amount of air processed through the trap (3). A container with a known volume was evacuated and the absolute pressure recorded with a pressure gauge. A four-way ball valve controlled the flow of the air into this "fixed-volume" container. A measured change in pressure within this tank corresponded to a specific volume of air passing through the freeze-out trap and into the container. Equation 1 was used to calculate the actual volume of sampled air:

$$V_s = \frac{\Delta P \; T_{std} \; V_c}{P_{std} \; T_c} \qquad (1)$$

where V_s = actual volume sampled
ΔP = change in pressure within the container
T_{std} = 298 K
V_c = volume of container as measured by water displacement
P_{std} = 1 atmosphere
T_c = temperature of the container.

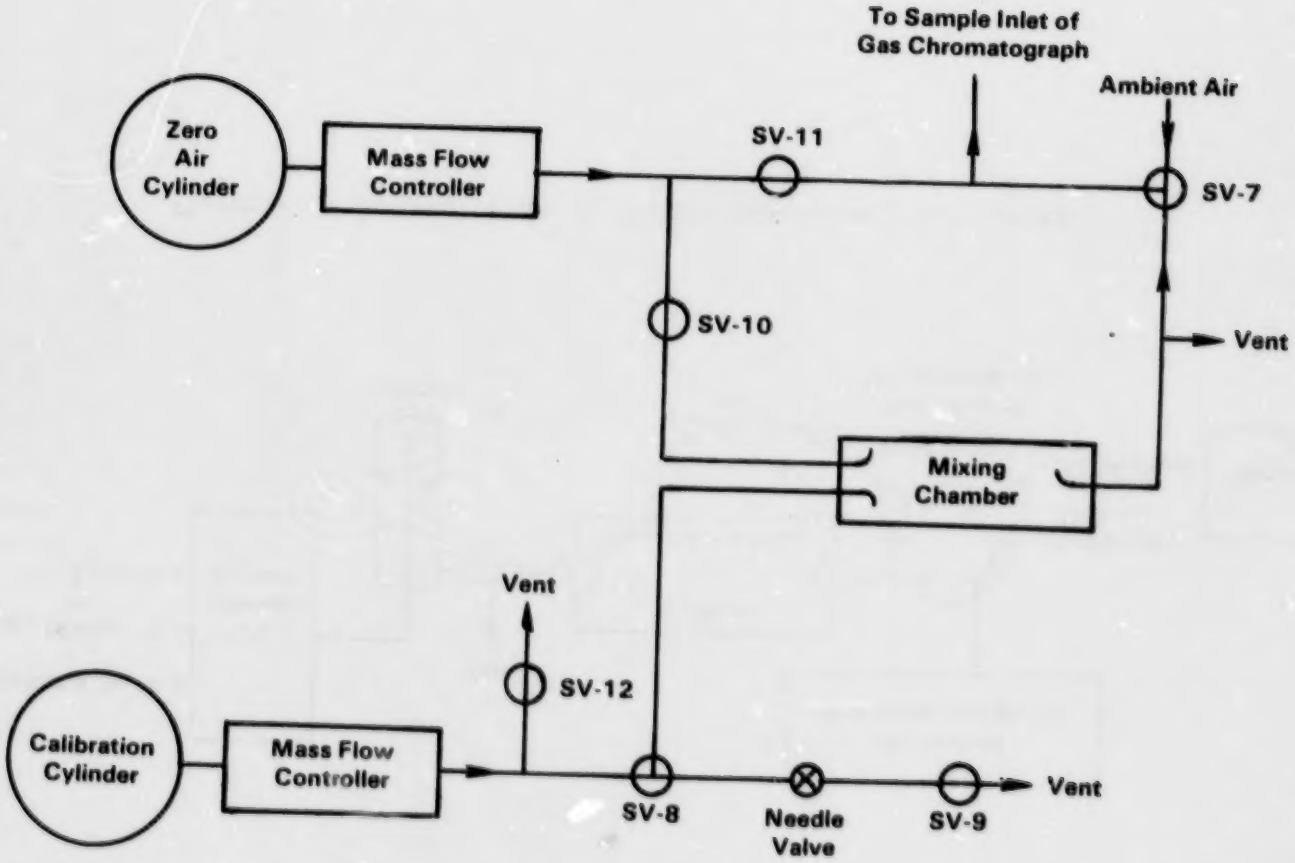

Figure 2. Diagram of flow scheme in prototype calibrator.

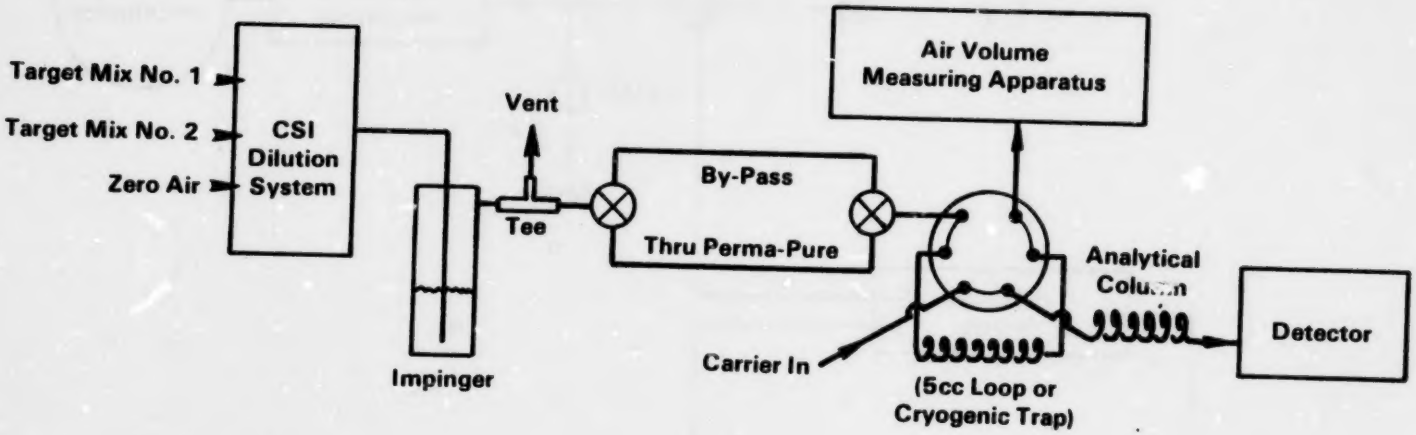

Figure 3. Experimental set-up for the Perma-Pure dryer studies.

Interference Studies

Ozone and nitrogen dioxide interference studies also made use of the CSI dilution system. The unit was modified so that the target mixture would enter through one mass flow controller while nitric oxide gas simultaneously passed through the other controller. With the unit in the gas-phase titration mode, various ozone concentrations were generated and served to oxidize the incoming nitric oxide to nitrogen dioxide. The nitrogen dioxide, excess ozone, and target compounds were then directed through a mixing chamber and exhausted to the gas chromatographic system for analysis. Ozone concentrations examined were 0, 100, 200, and 300 ppb. Nitrogen dioxide concentrations remained at 250 ppb while target compound concentrations ranged from 0.9 ppb for hexachlorobutadiene to 17.3 ppb for trichlorotrifluoroethane. Gas chromatographic sampling made use of the cryogenic trapping procedure and sample volumes of 200 mL were processed with the volume-measuring apparatus described earlier.

Automated System Intercomparison

Side-by-side comparisons of two essentially identical prototype automated sampling and analysis GC units were carried out using calibration mixtures and ambient air samples. Calibration comparison studies made use of the prototype calibrator to generate various concentrations of the target compounds. During the initial comparison, six record runs were performed for GC No. 1 while seven record runs were carried out on GC No. 2. An additional two record runs were completed in subsequent calibration tests. Each record run produced five calibration points for each of the sixteen target compounds listed in Table 7. The five calibration points include a zero concentration and nominal concentrations of 5, 10, 20 and 50 ppb. Actual concentrations were determined by measuring the calibration and dilution flows before and after a series of record runs. Sample flow through the cryogenic trap was maintained at 15 cc/min with a mass flow controller. A collection time of 10 minutes provided sufficient sample. Compound analyses were accomplished with flame ionization detectors.

The second phase of the intercomparison focused on simultaneous sampling from a common manifold with both GC units. During this testing period, three successive runs of laboratory air were processed by both instruments. Additionally, canister samples of ambient air were analyzed with both units. Figure 4 shows the configuration of the system during the intercomparison studies. This figure shows three subunits, the calibration unit, the sample handling system, and the preconcentration and analysis system. The calibration subunit consists of a dynamic dilution system using pressurized gas cylinders, electronic flow controllers (FC-L and FC-H) and valves. This subunit is explained in more detail in Reference 15. The sample handling system consists of a manifold with provision for obtaining either calibration air, spiked ambient or ambient air. The Perma-Pure dryer is also a part of this subunit. The third subunit (preconcentration and analysis system) is essentially the same as shown in Figure 1.

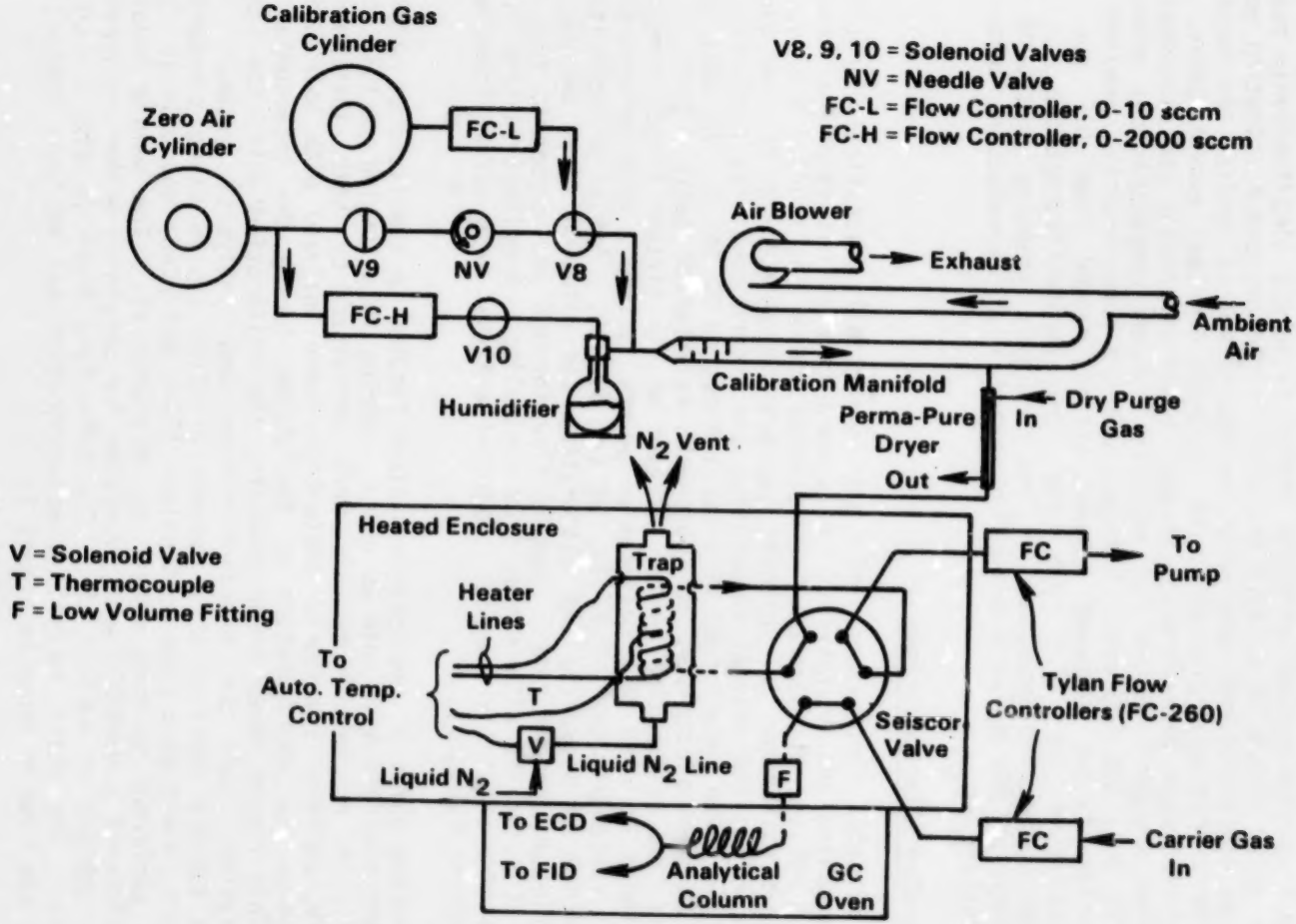

Figure 4. Configuration of automated GC system during intercomparison studies.

Sample Integrity Study with Stainless Steel Canisters

During the program the storage characteristics were determined for sixteen volatile organics (listed in Table 7) in stainless steel canisters (Demaray Scientific Instrument, Ltd., Pullman, WA). The system used to fill and sample from the canisters is shown in Figures 5 and 6. Figure 5 depicts the configuration employed during the canister filling cycle while Figure 6 illustrates the scheme utilized during the canister analysis cycle.

Prior to filling the canisters with the target mixture, the above assembly was checked to insure that the system did not contribute contaminant peaks to the sample. Zero air was sampled directly from the manifold and compared with zero air passing through the canister filling station.

Seven canisters were pressurized with a prepared gaseous mixture (16 organics) at a nominal concentration of 2 ppb. Air samples were taken from each canister at 0, 2, 4 and 7 days after filling. During the initial filling period nine air samples were also taken directly from the manifold system and analyzed in real time. For discussion purposes, these real time samples will be referred to as control samples.

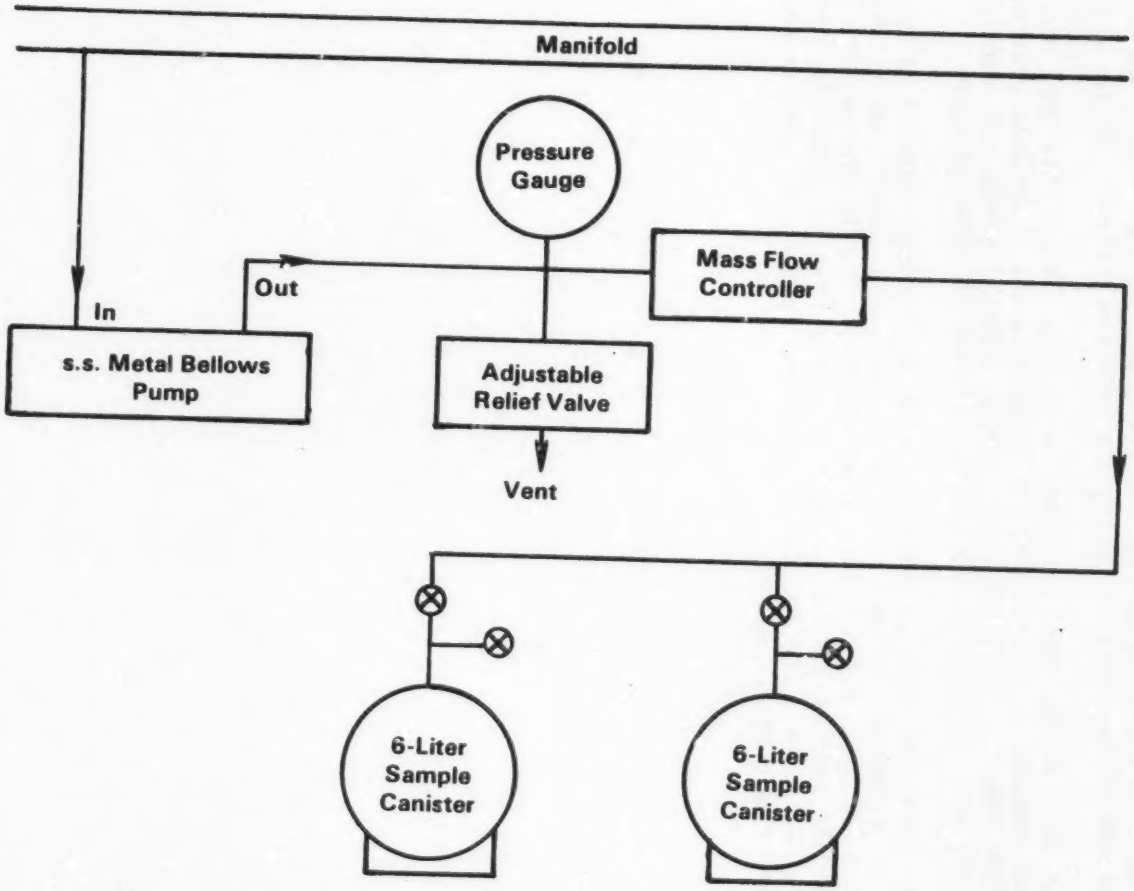

Figure 5. Canister apparatus during sample fill cycle.

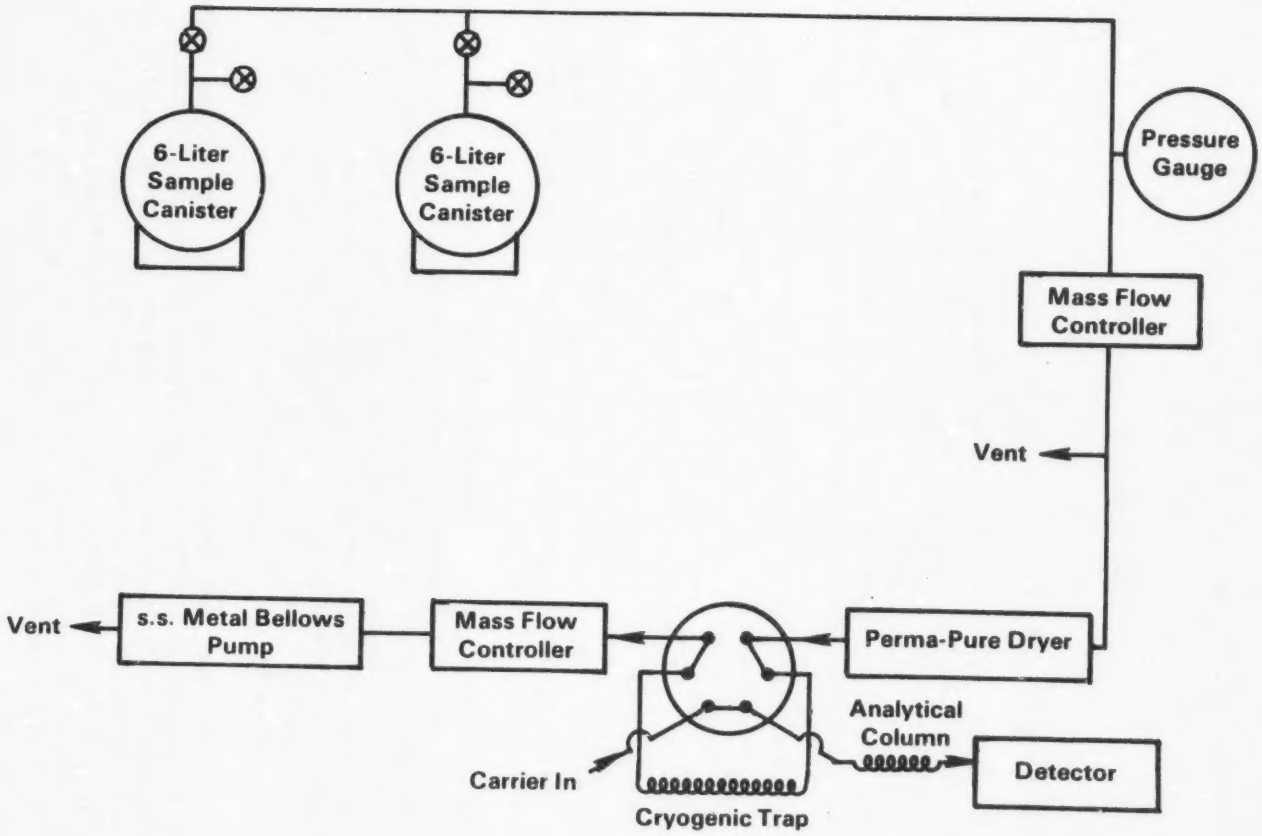

Figure 6. Canister apparatus during sample analysis cycle.

SECTION 5

RESULTS AND DISCUSSION

BASIC LABORATORY STUDIES

Figure 7 shows several calibration mixture chromatograms that were processed with the automated sampling and analysis system. Table 1 depicts the mean concentration and standard deviation for each of the eight eluting compounds. As the data indicate, excellent precision was obtained. Furthermore, the sampling process was easily initiated and terminated by single keystroke commands. No additional operator involvement was needed.

The above operations were carried out with a dry calibration mixture. Additional experiments under humidified conditions showed that water vapor had a significant effect upon the chromatography of the sample components. Table 2 shows the data from a test mixture that was processed under dry and humidified conditions. Excellent retention time reproducibility was obtained for those compounds when the sampling stream was dry. However, when water vapor was also present, standard deviations of compound retention times were significantly greater. When gas chromatography is the only instrumentation available for analysis, this retention time variability makes positive peak identification extremely difficult.

The trend of increased variability with shorter retention times in Table 2 is typical when cryogenically trapped compounds including water are transferred from the trap to a capillary column held at reduced temperature. The column is blocked temporarily by ice until the column temperature is increased. The time delay interval is a smaller fraction of the retention time for compounds eluting last. Therefore, the erratic nature of the blocking process causes increased variability in retention time for those compounds eluting early in the chromatographic run.

Tables 3 to 5 show the results of tests with the Perma Pure dryer. These tests were carried out with two prototype GC systems (Battelle and EPA systems). Both units were used to test a common subset of target compounds although not all compounds were common to both tests (Tables 3 and 4). The Battelle results (Table 3) indicate that for a humidified sample there is no significant difference between results with and without the dryer. The same can be said for a dry sample with the exception of benzylchloride. However, dry sample results were significantly lower than humid sample results for at least three gases: 1,3-dichloropropene(cis), 1,2-dibromoethane, and benzylchloride. To investigate this effect further and to obtain a measure of variability for replicate analytical runs, additional tests were performed at EPA. The EPA results shown in Table 4 verify the Battelle results but show no

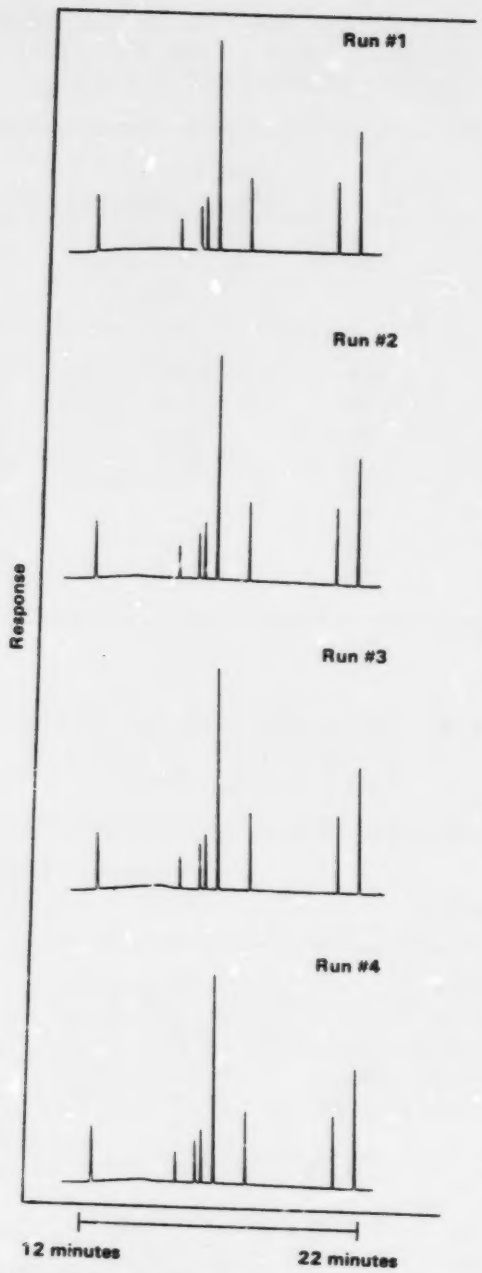

Figure 7. Automated chromatographic analyses of a standard mixture using cryogenic preconcentration techniques and flame ionization detection (100 mL sample).

TABLE 1. STATISTICAL ANALYSES OF CHROMATOGRAMS SHOWN IN FIGURE 7 (TEST 1) AND ADDITIONAL ANALYSIS AT LOWER CONCENTRATIONS (TEST 2)

Compound	Test 1 (4 runs, 200-mL samples) Mean (ppbv)	Test 1 (4 runs, 200-mL samples) Coefficient of variation (%)	Test 2 (8 runs, 200-mL samples) Mean (ppbv)	Test 2 (8 runs, 200-mL samples) Coefficient of variation (%)
Vinylidene chloride	144	4.4	6.1	3.9
Chloroform	84	3.8	3.5	5.8
1,2-Dichloroethane	44	3.7	1.9	5.1
Methylchloroform	63	4.5	2.7	4.9
Benzene	93	4.0	3.9	5.1
Trichloroethylene	84	3.7	3.5	4.1
Tetrachloroethylene	69	3.7	2.9	4.3
Chlorobenzene	46	3.3	1.9	3.2

TABLE 2. RETENTION TIMES FOR SEVERAL COMPOUNDS CRYOGENICALLY COLLECTED AND ANALYZED UNDER DRY AND HUMIDIFIED CONDITIONS[a]

Compound	Retention Time, Minutes[b] Dry[c]	Retention Time, Minutes[b] Humidified[d]
Chloroform	11.61 ± 0.01	11.82 ± 0.28
Methylchloroform	12.50 ± 0.01	12.66 ± 0.22
Carbon tetrachloride	13.09 ± 0.00	13.22 ± 0.18
Trichloroethylene	14.12 ± 0.01	14.21 ± 0.12
Tetrachloroethylene	17.27 ± 0.00	17.30 ± 0.04

a 200-mL air samples analyzed via electron capture detection.
b Average ± standard deviation.
c Average of three runs at <100 ppm water vapor.
d Average of four runs at 27% RH and 27 C.

TABLE 3. SAMPLE INTEGRITY RESULTS WITH A PERMA PURE DRYER FOR THOSE TARGET COMPOUNDS RESPONDING TO A FLAME IONIZATION DETECTOR[a] --BATTELLE RESULTS

Compound[b]	Dry Sample[c]		Humidified Sample[d]	
	Through Dryer	Dryer Bypassed	Through Dryer	Dryer Bypassed
Trichlorotrifluoroethane	259 ± 1	259 ± 1	255 ± 1	253 ± 1
Chloroform	79 ± 1	79 ± 1	80 ± 2	80 ± 2
1,2-Dichloroethane	50 ± 4	50 ± 3	54 ± 1	56 ± 1
Methylchloroform	61 ± 1	62 ± 1	63 ± 1	60 ± 1
Benzene	92 ± 2	90 ± 2	93 ± 1	95 ± 1
Carbon tetrachloride	126 ± 1	124 ± 1	123 ± 1	122 ± 1
Trichloroethylene	82 ± 1	81 ± 1	80 ± 1	82 ± 1
1,3-Dichloropropene (cis)	175 ± 5	166 ± 6	203 ± 3	199 ± 1
Toluene	245 ± 1	243 ± 2	251 ± 3	248 ± 1
1,2-Dibromoethane	124 ± 3	116 ± 3	153 ± 5	148 ± 1
Tetrachloroethylene	67 ± 1	67 ± 1	67 ± 1	67 ± 1
Chlorobenzene	46 ± 2	39 ± 3	49 ± 1	51 ± 1
o-Xylene	146 ± 2	145 ± 2	151 ± 2	149 ± 1
Benzylchloride	17 ± 2	10 ± 2	58 ± 4	56 ± 1
Hexachlorobutadiene	26 ± 1	25 ± 1	29 ± 1	31 ± 1

a Each concentration reported represents the average in ppb for two runs; a five mL sample loop was used.
b Vinylidene chloride was not measured in this experiment because of excessive peak broadening due to the size of the sample loop.
c <100 ppm water vapor.
d 83% RH at 23 C.

TABLE 4. SAMPLE INTEGRITY RESULTS WITH A PERMA PURE DRYER FOR COMPOUNDS RESPONDING TO A FLAME IONIZATION DETECTOR[a] --EPA RESULTS

Compound	Dry Sample[b]		Humidified Sample[c]
	Through Dryer	Dryer Bypassed	Through Dryer[d]
Vinyl chloride	1076 ± 32	1106 ± 8	1063 ± 11
Dichloroethylene	1085 ± 14	1096 ± 7	1118 ± 73
Trichlorotrifluoroethane	1019 ± 8	1015 ± 7	1038 ± 18
Chloroform	391 ± 4	391 ± 4	391 ± 5
1,2-Dichloroethane	1003 ± 19	1025 ± 11	1026 ± 19
Methylchloroform	1368 ± 6	1348 ± 16	1367 ± 10
Benzene	2816 ± 23	2943 ± 20	2748 ± 21
Carbon tetrachloride	331 ± 3	332 ± 2	340 ± 5
Trichloroethylene	1184 ± 10	1182 ± 9	1192 ± 5
1,3-Dichloropropene (cis)	854 ± 14	870 ± 8	876 ± 6
1,3-Dichloropropene (trans)	683 ± 24	693 ± 17	728 ± 4
Toluene	3605 ± 38	3657 ± 22	3507 ± 36
1,2-Dibromoethane	1059 ± 24	1070 ± 10	1083 ± 6
Tetrachloroethylene	1247 ± 9	1251 ± 15	1260 ± 10
Chlorobenzene	3393 ± 31	3353 ± 30	3408 ± 16
Benzylchloride	3062 ± 439	3046 ± 223	3435 ± 62
Hexachlorobutadine	1992 ± 162	1805 ± 61	1932 ± 83
o-Xylene	4136 ± 36	4185 ± 33	4042 ± 24

a Concentrations are nominally 100 ppbv; 9 replicate runs for dry samples, 12 for humidified samples. Cryogenic preconcentration of 938 mL, concentration (± standard deviation) measured in area counts.
b Less than 0.2% water vapor in air, room temperature approximately 25 C.
c 1.9 ± 0.1% water vapor in air, room temperature approximately 25 C.
d No humidified samples were analyzed without the dryer because water plugs the capillary column.

TABLE 5. SAMPLE INTEGRITY RESULTS WITH A PERMA PURE DRYER FOR COMPOUNDS RESPONDING TO AN ELECTRON CAPTURE DETECTOR[a]

Compound	Dry Sample[b]		Humidified Sample[c]	
	Through Dryer	Dryer Bypassed	Through Dryer	Dryer Bypassed
Trichlorotrifluoroethane	375	345	376 ± 60	378 ± 40
Chloroform	213	213	215 ± 3	219 ± 3
Methylchloroform	290	287	251 ± 13	274 ± 9
Carbon tetrachloride	660	660	630 ± 21	655 ± 28
Trichloroethylene[d]	-	-	-	-
1,3-Dichloropropene (cis)	900	900	933 ± 35	950 ± 35
1,2-Dibromoethane	640	659	640 ± 13	653 ± 6
Tetrachloroethylene	318	318	316 ± 7	313 ± 14
Hexachlorobutadiene	130	145	140 ± 3	138 ± 7

a A single analysis was made during the dry sample experiment; duplicate analyses were performed during the humidified experiments. A five mL sample loop was used and concentration is in pptv.
b 100 ppm water vapor.
c 80% RH at 25 C.
d Contamination in stream selecting valve.

evidence of a difference between results for dry and humid samples. All but one of the standard deviation values are less than ten percent of the mean and most are less than five percent of their respective means. Benzylchloride shows the highest standard deviation values. One reason for this variability was obvious when the analytical results were plotted in sequence. Significant delays in establishing equilibrium concentration levels were observed for some of the compounds in changing from one type of test to another, i.e., from a dry sample to a humidified sample. These effects probably are the reason for the differences between wet and dry sample test results in the data in Table 3.

Table 5 presents the results of experiments in which the CSI dilution system was used to generate ppt levels of the target compounds and an electron capture detector was employed for analysis. No significant difference was observed between the humidified and dry streams and again the overall data indicated the Perma Pure dryer did not affect the integrity of the target compounds.

Cryogenic collection and recovery efficiency studies of the target compounds were carried out by comparing the peak area response values obtained by the direct sample loop injections to the values found by cryogenic preconcentration of dilute sample streams. The target compounds that were examined, along with their concentrations, are listed in Table 3. Humidified sample air was passed through the Perma Pure dryer, the 5 mL loop and then analyzed by gas chromatographic/flame ionization detection techniques. The same air was subsequently diluted 1/100 fold with humidified zero air, passed through the dryer, directed to a reduced-temperature trap (200 mL) and analyzed. When the dilution stream (1/100 fold) and concentration effects from the cryogenic collection procedure (200-mL samples) were accounted for, recovery efficiencies of 100 $\pm$ 5 percent were obtained for all the compounds. This recovery is within the estimated experimental error of $\pm$10 percent and consisted primarily of errors in determining gas dilution and sample volumes.

The results from the four ozone and nitrogen dioxide interference tests are depicted in Table 6. Test 1 was conducted without the addition of ozone and nitrogen dioxide. During tests 2 to 4 ozone concentrations were 100, 200, or 300 ppb and the nitrogen dioxide level was maintained at 250 ppb. As the data indicate, none of the target compounds was affected by the presence of ozone or nitrogen dioxide. Furthermore, no artifact peaks or deleterious column effects were observed during or subsequent to these tests. Although the above experiments were certainly not exhaustive, the generated concentrations were construed to be realistic atmospheric levels. The results allowed us to conclude that the cryogenic trapping techniques and instrumentation employed in this study did not significantly affect the sample integrity of the target compounds. An effective detection limit of at least 0.1 ppb per compound was obseved during these tests, based on a 200-mL sample and flame ionization detection. Lower detection limits could be achieved for many of these compounds by employing more sensitive detectors such as the electron capture or photoionization detection system.

TABLE 6. OZONE AND NITROGEN DIOXIDE INTERFERENCE RESULTS USING FLAME IONIZATION DETECTION[a]

Compound	Concentration in Given Test, ppbv			
	1	2	3	4
Ozone	0	100	200	300
Nitrogen Dioxide	0	250	250	250
Vinylidene Chloride	8.7	8.8	8.8	9.1
Trichlorotrifluorethane	17.3	17.0	17.0	16.8
Chloroform	4.8	5.1	5.1	5.2
1,2-Dichloroethane	3.1	3.2	3.1	3.2
Methylchloroform	3.8	3.8	3.8	4.0
Benzene	5.7	5.7	5.7	5.9
Carbon tetrachloride	7.8	7.9	8.0	7.9
Trichloroethylene	4.8	5.0	5.0	5.2
1,3-Dichloropropene	9.7	9.4	9.7	8.7
Toluene	14.2	14.1	14.5	14.2
1,2-Dibromoethane	6.7	6.9	7.1	7.2
Tetrachloroethylene	4.1	4.1	4.1	4.3
Chlorobenzene	2.9	3.0	3.1	3.2
o-Xylene	7.2	7.5	7.8	7.5
Benzylchloride	1.3	1.3	1.4	1.4
Hexachlorobutadiene	0.9	0.9	1.0	1.1

[a] 200 mL samples with cryogenic trapping.

Software Development

Following the basic laboratory studies, research efforts primarily focused on developing software to carry out the monitoring and calibration needs of the automated GC sampling and analysis system. In addition to facilitating zone heating and cooling, sample collection and injection, chromatographic run conditions and data processing, the basic software permitted three essential modes of GC operation:

- calibration
- ambient air
- calibration and ambient air.

In the calibration mode of operation either single or multipoint calibrations can be carried out. The single point subroutine results in one zero air run plus one or more runs (up to 10) of a single dilution mixture. The multipoint calibration subroutine includes one zero air run followed by runs of four different dilution mixtures. After the completion of either calibration subroutine, a linear regression analysis is performed on each compound of interest. A linear regression equation along with the correlation coefficient and the number of analyses are given as output parameters for each compound. However following the initial use of the program, the correlation coefficient was found to be a poor indicator of calibration linearity. In future work, it will be replaced by some other parameter such as the mean square error. A printout of the current program is given in Appendix A.

Presently, the system's calibration table is not accessible from the BASIC program (to do this would require knowledge of the HP operating system). As a result, once the calibration procedure is completed, the appropriate compound response factors are manually inputted to the GC's existing calibration table in preparation for ambient air sampling.

The ambient air mode of operation can be conducted with or without calibration (operator controlled). After each run is completed (ambient and/or calibration), a GC report is printed and then transferred to a cassette for future use. This transfer process conserves space in the system memory so that an unlimited number of ambient air samples can be processed.

With the current program the operator does not have to be present to start sample collection. When the mode of instrument operation is initialized, the operator simply specifies the start time needed (24 hour clock). The start time option can also be easily modified so as to delay initiation of sample collection by one or more days. Likewise with the current software, the primary GC functions (i.e., sample collection and analysis) take place sequentially. In order to provide for a more extended time coverage during real-time field sampling, the program can be modified so that sample collection for the "next" run is initiated during the analysis of the current run. By incorporating this modification along with a second automated GC system, one can sample ambient air with essentially complete time coverage.

Automated System Intercomparison

Side-by-side comparison of two prototype automated GC units were carried out using calibration mixtures and ambient air samples. During the initial calibration studies, results gave non-linear calibration curves from both GC units. Since the GC units were expected to perform in a linear fashion (when using a flame ionization detector) we suspected that the prototype calibrator might be malfunctioning. Several modifications were subsequently made to the calibrator unit and closer scrutiny of the actual calibration and dilution flow measurements were carried out during the second series of tests.

The statistical treatment of the data from the second calibration period was as follows. The five calibration points from each record run were used to form a calibration line. The calibration line was found by regressing concentration (C) on raw area (RA) and determining the least squares regression line. For a particular record run, let a and b denote the intercept and slope, respectively, of the calibration line. For each of the calibration points, an estimated concentration, $\hat{C}$, was obtained from the formula

$$\hat{C} = a + b\,(RA)$$

The process of forming a calibration line and calculating estimated concentrations was repeated for each record run. Thus each calibration point (C, RA) has associated with it an estimated concentration $\hat{C}$ and an error in estimation

$$E = \hat{C} - C$$

The error in estimation, E, is the absolute error. Also of interest is the relative error in estimation

$$RE = (\hat{C} - C)/C = E/C \quad .$$

Table 7 lists the 16 target compounds that were analyzed in the above fashion. Actual data from 1,2-dichloroethane (flame ionization detector) are depicted in Tables 8 and 9. A percent relative error of less than 10 was obtained during both calibration runs. Similar relative errors were also obtained with both GC units for 13 of the remaining 15 compounds. The two exceptions, benzyl chloride and hexachlorobutadiene, exhibited RE values of ∿20 percent at the lowest non-zero concentration level (∿4 ppbV).

The above results indicate good linear behavior of both GC systems (using flame ionization detection) and demonstrate the capability of these instruments to accurately determine low ppb concentrations of ambient air species. However it is felt that even better detection levels can be achieved. From Tables 8 and 9 intercepts of 0.54 ppb and 0.75 ppb are observed for both calibration runs from instrument No. 1 and intercept values of 0.35 ppb and 0.57 ppb are obtained for the second GC unit. Both instruments behave similarly during each calibration run when viewing the percent relative errors at each concentration. Based on the actual signal to noise ratios of ∿30/1 at the 4 ppb level, lower intercept values were expected. Flow measurement errors may account for the higher than expected intercepts; likewise partial sample adsorption within the calibrator itself

TABLE 7. LIST OF TARGET COMPOUNDS EXAMINED DURING CALIBRATION RUNS

Propane	Trichloroethylene
Vinyl Chloride	1,3-Dichloropropene (cis)
Vinylidene Chloride	1,3-Dichloropropene (trans)
Trichlorotrifluoroethane	1,2-Dibromoethane
Chloroform	Tetrachloroethylene
1,2-Dichloroethane	Chlorobenzene
Methyl Chloroform	Benzyl Chloride
Carbon Tetrachloride	Hexachlorobutadiene

TABLE 8. DATA OBTAINED FROM THE STATISTICAL ANALYSIS OF A MULTIPOINT CALIBRATION RUN (1,2-DICHLOROETHANE) WITH GC NO. 1

Regression Equation	Calibration Run No.	Conc ppb	Raw Area	Estimated Conc ppb	Error	% Relative Error
(C)=0.5395+ 0.8769(RA)	1	0.00	0.00	0.54	-0.54	-
	1	4.04	3.61	3.71	0.33	8.2
	1	9.90	10.57	9.81	0.09	0.9
	1	19.80	21.68	19.55	0.25	1.3
	1	49.30	55.76	49.44	-0.14	-0.3
(C)=0.7470+ 0.9104(RA)	2	0.00	0.00	.75	-0.75	-
	2	3.88	3.72	4.13	-0.25	-6.4
	2	10.10	9.36	9.27	0.83	8.2
	2	20.00	20.63	19.53	0.47	2.4
	2	50.40	54.87	50.70	-0.30	-0.6

TABLE 9. DATA OBTAINED FROM THE STATISTICAL ANALYSIS OF A MULTIPOINT CALIBRATION RUN (1,2-DICHLOROETHANE) WITH GC NO. 2

Regression Equation	Calibration Run No.	Conc ppb	Raw Area	Estimated Conc ppb	Error	% Relative Error
(C)=0.3519+ 0.5604(RA)	1	0.00	0.00	0.35	-0.35	-
	1	4.04	5.91	3.66	0.30	9.30
	1	9.90	17.14	9.96	-0.06	-0.58
	1	19.80	34.56	19.72	0.08	0.40
	1	49.30	87.42	49.35	-0.05	-0.09
(C)=0.5663+ 0.5786(RA)	2	0.00	0.00	0.57	-0.57	-
	2	3.88	5.97	4.02	-0.14	-3.62
	2	10.10	14.98	9.23	0.86	8.57
	2	20.00	33.64	20.03	-0.03	-0.15
	2	50.40	86.35	50.53	-0.13	-0.26

may also contribute to the "non-zero" intercept. In many cases, a better fit of the calibration data was actually obtained with a quadratic curve. Unfortunately, the GC system's calibration table only permits the entry of a slope value (compound response factor). Efforts to modify the system's calibration table to accept non-linear curves were beyond the scope of this contract.

Automated System Intercomparison Using Laboratory Air

The second phase of the intercomparison focused on simultaneous sampling from a common manifold with both GC units. One of the data sets is shown in Table 10. Eight of the target compounds were identified and quantitated with both GCs. The chlorinated species were measured with electron capture detection while the aromatic species were determined by flame ionization detection. As the data indicate, reasonable agreement between the two GC units was obtained. Deviations from the mean for the 24 comparisons ranged from 0.0 to 20.5 percent.

Statistical Analysis of Canister Data

The purpose of the statistical analysis of the canister data was to evaluate the stability of samples stored in canisters and consequently to compare the data from the samples stored in canisters to data from control samples. Table 7 lists the sixteen compounds that were statistically treated during the canister tests. (Appendix B lists the raw area values for the canister samples). Sample means and standard deviations for the canister data are reported by compound in Table 11. Each of the SAMEDAY, DAY2, DAY4, and DAY7 means represent the average of seven raw areas, one from each of seven canisters (except in the cases noted). Sample standard deviations are reported in parentheses.

The primary quantities of interest for the canister data are the percent relative biases (PRB) introduced by storing samples in the canisters. For each of days 2, 4, and 7, the percent relative bias for day i is defined as

$$PRB_i = \left[\frac{(\text{True average raw area for canister samples on day } i)}{(\text{True average raw area for samples on day } 0)} - 1 \right] \times 100 \quad .$$

Estimates of the percent relative biases are reported in Table 12 with 99 percent confidence intervals reported in parentheses. A confidence level of 99 percent was chosen because of the large number of confidence intervals being formed. If the confidence interval for a PRB does not contain zero, this is an indication of a bias that is significantly different from zero.

To arrive at the confidence intervals in Table 12, the data for each compound were analyzed using a randomized complete block model (canisters represent blocks and sampling time represents the treatments). Dunnett's procedure was used to obtain simultaneous 99 percent confidence intervals for the true average raw area difference between days 2, 4, and 7 and day 0 (16). The endpoints of these intervals were then divided by the SAMEDAY mean and multiplied by 100 to arrive at the confidence intervals in Table 12.

TABLE 10. COMPARISON OF TWO AUTOMATED GC UNITS SAMPLING SIMULTANEOUSLY FROM A COMMON MANIFOLD[a]

Compound	GC Response During Given Run, ppbv								
	Run 1			Run 2			Run 3		
	GC 1	GC 2	%D[b]	GC 1	GC 2	%D	GC 1	GC 2	%D
Trichlorotrifluoroethane	0.16	0.18	5.9	0.24	0.24	0.0	0.23	0.24	2.1
Chloroform	0.15	0.20	14.3	0.43	0.48	5.5	0.57	0.60	2.6
Methylchloroform	0.49	0.56	6.7	0.71	0.75	2.7	0.64	0.66	1.5
Carbon tetrachloride	0.15	0.16	3.2	0.21	0.19	5.0	0.20	0.18	5.3
Trichloroethylene	0.29	0.44	20.5	0.64	0.75	7.9	0.76	0.68	5.6
Tetrachloroethylene	1.25	1.47	8.1	4.79	5.37	5.7	4.63	5.00	3.8
Benzene	0.72	c	-	0.77	c	-	0.91	c	-
Toluene	3.40	3.49	1.3	7.17	7.56	2.6	9.29	9.52	1.3
O-xylene	1.39	1.15	5.5	4.16	3.68	6.1	4.30	3.41	11.5

a 0.3 Liters of laboratory air collected with cryogenic preconcentration techniques (23 C, 40 % RH).
b Percent deviation from the mean.
c Indicates a co-eluting interferant.

TABLE 11. SAMPLE MEANS AND STANDARD DEVIATIONS FOR CANISTER SAMPLE RAW AREA VALUES

Compound	Sameday Mean	(S.D.)	Day 2 Mean	(S.D.)	Day 4 Mean	(S.D.)	Day 7 Mean	(S.D.)
Propane	2.73	(0.090)	2.75	(0.073)	2.73	(0.042)	2.78	(0.014)
Vinyl Chloride	1.83	(0.075)	1.85	(0.040)	1.81	(0.053)	1.89	(0.119)
Vinylidene Chloride	2.07	(0.040)	2.16	(0.019)	2.14	(0.034)	2.16	(0.008)
Trichlorotrifluoroethane	1.93	(0.025)	1.97	(0.051)	1.95	(0.045)	1.98	(0.041)
Chloroform	1.93	(0.086)	2.01	(0.071)	1.99	(0.046)	1.96	(0.047)
1,2 Dichloroethane	1.86	(0.070)	1.89	(0.040)	1.86	(0.030)	1.87	(0.045)
Methyl Chloroform	1.93	(0.037)	1.97	(0.022)	1.96	(0.016)	1.95	(0.020)
Carbon Tetrachloride	2.01	(0.025)	2.04	(0.075)	2.09	(0.046)	2.00	(0.033)
Trichloroethylene[a]	1.78	(0.077)	1.83	(0.045)	1.84	(0.049)	1.81	(0.027)
1,3 Dichloropropene (cis)[b]	0.82	(0.035)	0.77	(0.041)	0.75	(0.064)	0.76	(0.030)
1,3 Dichloropropene (trans)[b]	0.64	(0.036)	0.63	(0.075)	0.63	(0.061)	0.63	(0.061)
1,2 Dibromoethane[a]	1.36	(0.090)	1.37	(0.091)	1.35	(0.080)	1.38	(0.091)
Tetrachloroethylene	1.58	(0.059)	1.62	(0.042)	1.61	(0.047)	1.63	(0.035)
Chlorobenzene	1.39	(0.106)	1.43	(0.078)	1.41	(0.073)	1.43	(0.087)
Benzyl Chloride	1.01	(0.102)	0.94	(0.049)	0.94	(0.376)	0.82	(0.109)
Hexachlorobutadiene[a]	1.25	(0.319)	1.25	(0.232)	1.29	(0.313)	1.39	(0.417)

a Reported values based on data from six canisters.
b Reported values based on data from five canisters.

TABLE 12. POINT ESTIMATES AND 99 PERCENT CONFIDENCE INTERVALS FOR THE PERCENT RELATIVE BIAS ON DAYS 2, 4, AND 7

Compound	Day 2 Percent Relative Bias	(C.I.)[c]	Day 4 Percent Relative Bias	(C.I.)	Day 7 Percent Relative Bias	(C.I.)
Propane	0.7	(-3.4, 4.9)	0.0	(-4.1, 4.1)	1.8	(-2.3, 6.0)
Vinyl Chloride	1.1	(-6.0, 8.2)	-1.1	(-8.2, 6.0)	3.3	(-3.8,10.4)
Vinylidene Chloride	4.3	(1.7, 7.0)	3.4	(0.7, 6.0)	4.3	(1.7, 7.0)
Trichlorotrifluoroethane	2.1	(-1.0, 5.1)	1.0	(-2.0, 4.1)	2.6	(-0.5, 5.7)
Chloroform	4.1	(0.6, 7.7)	3.1	(-0.5, 6.7)	1.6	(-2.0, 5.1)
1,2 Dichloroethane	1.6	(-1.5, 4.7)	0.0	(-3.1, 3.1)	0.5	(-2.6, 3.6)
Methyl Chloroform	2.1	(-0.2, 4.3)	1.6	(-0.7, 3.8)	1.0	(-1.2, 3.3)
Carbon Tetrachloride	1.5	(-2.9, 5.9)	4.0	(-0.4, 8.4)	-0.5	(-4.9, 3.9)
Trichloroethylene[a]	2.8	(-2.1, 7.7)	3.4	(-1.5, 8.3)	1.7	(-3.2, 6.6)
1,3 Dichloropropene (cis)[b]	-6.1	(-13.2, 1.0)	-8.5	(-15.6,-1.5)	-7.3	(-14.4,-0.3)
1,3 Dichloropropene (trans)[b]	-1.6	(-14.2,11.1)	-1.6	(-14.2,11.1)	-1.6	(-14.2,11.1)
1,2 Dibromoethane[a]	0.7	(-2.9, 4.3)	-0.7	(-4.3, 2.9)	1.5	(-2.1, 5.1)
Tetrachloroethylene	2.5	(-0.3, 5.4)	1.9	(0.9, 4.7)	3.2	(0.3, 6.0)
Chlorobenzene	2.9	(0.1, 5.6)	1.4	(-1.3, 4.2)	2.9	(0.1, 5.6)
Benzyl Chloride	-6.9	(-41.2,27.3)	-6.9	(-41.2,27.3)	-18.8	(-53.1,15.5)
Hexachlorobutadiene[a]	0.0	(-17.8,17.8)	3.2	(-14.6,21.0)	11.2	(-6.6,29.0)

a Reported values based on data from six canisters.
b Reported values based on data from five canisters.
c 99 percent confidence interval.

Inspection of Table 12 shows that all the compounds, excluding vinylidene chloride, have no significant bias. Although the confidence intervals for vinylidence chloride do indicate a slight positive bias, the relative biases are less than five percent for this compound. For all sixteen compounds tested, concentrations after four days of storage were within ±8 percent of the initial values. However, after storage for seven days the average benzyl chloride concentration decreased by approximately 19 percent while hexachlorobutadience increased by approximately 11 percent. If the above results using calibration mixtures are extrapolated to ambient air samples, the passivated canisters should serve as acceptable temporary storage devices for the above target compounds.

For the purpose of comparing the canister data with the control sample data, the canister data was pooled across sampling times. The overall canister mean, standard deviation, and relative standard deviation (standard deviation times 100 divided by mean) and the corresponding values for the control samples are reported in Table 13. Each CONTROL mean and standard deviation is based on nine raw area values.

An estimated percent relative bias (PRB) is calculated for each compound using the formula

$$PRB = \left[\frac{\text{Canister Mean}}{\text{Control Mean}} - 1 \right] \times 100 \quad .$$

A 99 percent confidence interval for the PRB was calculated by first obtaining a confidence interval for the true average raw area difference (CANISTER-CONTROL) using standard statistical techniques. The endpoints were then divided by the CONTROL mean and multiplied by 100 to arrive at the confidence intervals in Table 13.

Examining the PRB estimates and confidence intervals in Table 13 shows a general tendency towards a positive bias. That is, on the average, the raw area values for canister samples tend to be larger than the raw area values for the control samples. For fourteen of the sixteen compounds tested, the positive bias ranges from 1 to 8 percent. Benzyl chloride and hexachlorobutadiene exhibit relative positive biases of 36 and 72 percent respectively. The slight positive bias observed for the fourteen compounds is not significant and may have been due to an error in determining sample volumes during the analysis of the control samples. The abnormally high positive bias of benzyl chloride and hexachlorobutadiene is most likely due to the overall difficulty in analyzing these two compounds because of their strong surface adsorptive characteristics.

TABLE 13. SUMMARY TABLE FOR COMPARISON OF CONTROL DATA WITH COMBINED CANISTER DATA

Compound	Control Mean	(S.D.)	(R.S.D.)[c]	Canister Mean	(S.D.)	(R.S.D.)	Percent Relative Bias	(C.I.)[d]
Propane	2.63	(0.150)	(5.7)	2.75	(0.062)	(2.3)	4.4	(-0.6, 9.5)
Vinyl Chloride	1.76	(0.088)	(5.0)	1.85	(0.080)	(4.3)	4.9	(0.1, 9.8)
Vinylidene Chloride	2.03	(0.105)	(5.2)	2.13	(0.046)	(2.2)	5.0	(0.5, 9.6)
Trichlorotrifluoroethane	1.81	(0.111)	(6.1)	1.96	(0.044)	(2.2)	8.2	(2.8,13.6)
Chloroform	1.87	(0.146)	(7.8)	1.97	(0.068)	(3.5)	5.4	(-1.5,12.4)
1,2 Dichloroethane	1.77	(0.148)	(8.4)	1.87	(0.047)	(2.5)	5.6	(-1.7,12.9)
Methyl Chloroform	1.88	(0.100)	(5.3)	1.95	(0.028)	(1.4)	3.9	(-0.8, 8.5)
Carbon Tetrachloride	1.96	(0.098)	(5.0)	2.04	(0.058)	(2.8)	3.9	(-0.7, 8.4)
Trichloroethylene[a]	1.72	(0.128)	(7.4)	1.82	(0.054)	(3.0)	5.5	(-1.1,12.1)
1,3 Dichloropropene (cis)[b]	0.76	(0.092)	(12.1)	0.78	(0.049)	(6.3)	2.1	(-9.0,13.2)
1,3 Dichloropropene (trans)[b]	0.62	(0.087)	(14.0)	0.63	(0.055)	(8.7)	1.7	(-12.1,15.5)
1,2 Dibromoethane[a]	1.27	(0.142)	(11.2)	1.36	(0.083)	(6.1)	7.4	(-2.8,17.6)
Tetrachloroethylene	1.50	(0.140)	(9.3)	1.61	(0.048)	(3.0)	7.2	(-1.0,15.4)
Chlorobenzene	1.31	(0.142)	(10.8)	1.42	(0.084)	(5.9)	8.2	(-1.6,18.1)
Benzyl Chloride	0.68	(0.140)	(20.6)	0.93	(0.204)	(21.9)	36.1	(13.1,59.1)
Hexachlorobutadiene[a]	0.75	(0.121)	(16.1)	1.29	(0.310)	(24.0)	72.4	(46.6,98.2)

a Canister data based on six canisters.
b Canister data based on five canisters.
c Relative standard deviation (percent).
d 99 percent confidence interval.

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APPENDIX A

AUTOMATED GC SYSTEM SOFTWARE

Documentation for Autosampling Program (description of subroutines)

Valve Lister -- Lists position of system valves

Flush -- Configures valves to flush calibrator with zero gas

Gas 4, Gas 3, Gas 2, Gas 1 -- Configures calibrator to produce a specific span gas concentration

Ambient Config -- Configures calibration to sample ambient air

Injection Sub -- Collects and injects a gas sample

Parameter Change Delay -- Allows a delay during which system parameters can be altered

Valve Offer -- Turns all 12 valves off

Single Point Select -- Prompts for information needed to run a single point calibration

Single Point Run -- Runs single point calibration

Sum Var Init -- Sets all summation variables to zero

Lin Reg Sub -- Performs a linear regression

Peak Finder -- Identifies peaks associated with a calib table

Summer Sub -- summation of linear regression variables is performed

Fid Sub -- Displaced portion of Fid Tester Subroutine

Reporter Sub -- Creates calibration report on printer

ECD Sub -- Controls electron capture detector calibration data handling

Start on Time -- Allows run to be prepared ahead of time then begun at a specified time of day

FID Tester -- Controls flame ionization detector calibration data handling

Zero Pointer -- Zero gas run data handling utility
subroutine used by peak finder

F Values	Description of F/T Values in Program
1	List Valves 1 = yes
2	Trace Program 1 = yes
3	# of ambient samples
4	Calibrate? 1 = yes
5	Indicates which point is to be run (in single point mode)
6	# of repetitions during single point mode
7	1 = single point calibration
8	Which valve is actuated for the single point
9-17	Unused
18	Temporary storage for dilution factor for single point calibration
19	Number of points for linear regression
20	Dilution factor for calculation
21	Clock time for the start on time subroutine
22	Desired start time
23	Set to 1 if Q is used
24-26	Unused
27	Specifies which detector for placement in arrays
28	# of compounds found on a particular detector
29	Specifies "titles" of ECD files on tape
30	Indicates to certain subs if the run is a zero gas run

T Values	
1	Collection time
2	Calibrator flush time
3	Not used
4	Trap flush time
5	Trap cool down time

```
10   REM ********************************************AUTO SAMPLING PROGRAM
20   SYNC ON
30   INPUT "GET TABLES?....(Y/N)   ",A$
40   IF A$="N" THEN 110
50   PRINT "GETTING RUN TABLE"
60   GET RUN TBL 1 DEVICE# 16
70   PRINT "GETTING CALIBRATION TABLE"
80   GET CALIB 1 DEVICE# 16
90   PRINT "GETTING REPORT TABLE"
100  GET REPORT TBL 1 DEVICE# 16
110  PRINT "CLOSING ALL VALVES"
120  GOSUB 1860
130  PRINT "WELCOME TO THE AUTOSAMPLING PROGRAM"
140  DIM F(30),X(10,20),M(2,20),B(2,20),R(2,20)
150  DIM C(20)
160  FOR I=1 TO 20
170  READ C(I)
180  NEXT I
190  DATA 10000,10000,10000,10000,10000,10000,10000,10000,10000,10000
200  DATA 5000,5000,10000,10000,10000,10000,10000,10000,10000,0
210  FOR I=1 TO 5
220  READ D(I)
230  NEXT I
240  DATA 0, 0.00575, 0.00234, 0.00123, 0.000485
250  DATA PROPANE,VINYL CHLORIDE,VINYLIDENE CHLORIDE
260  DATA TRICHLOROTRIFLUOROETHANE,CHLOROFORM,1-2 DICHLOROETHANE
270  DATA METHYLCHLOROFORM,BENZENE,CARBON TETRACHLORIDE
280  DATA TRICHLOROETHYLENE,1-3 DICHLOROPROPENE(CIS)
290  DATA 1-3 DICHLOROPROPENE(TRANS),TOLUENE,1-2 DIBROMOETHANE
300  DATA TETRACHLOROETHYLENE,CHLOROBENZENE,O-XYLENE
310  DATA BENZYL CHLORIDE,HEXACHLOROBUTADIENE
320  DATA TRICHLOROTRIFLUOROETHANE,CHLOROFORM,METHYLCHLOROFORM
330  DATA CARBON TETRACHLORIDE,TRICHLOROETHYLENE
340  DATA 1-2 DIBROMOETHANE,TETRACHLOROETHYLENE,HEXACHLOROBUTADIENE
350  FOR I=1 TO 30
360  F(I)=0
370  NEXT I
380  INPUT "DO YOU WISH TO CALIBRATE DURING THIS RUN? (Y/N)  ",A$
390  IF A$="O" THEN 1070
400  IF A$="Y" THEN 430
410  INPUT "HOW MANY AMBIENT SAMPLES TO BE ANALYZED IN THIS RUN?   ",F(3)
420  GOTO 470
430  F(4)=1
440  INPUT "SINGLE OR MULTIPOINT? (S/M) ",A$
450  IF A$="M" THEN 470
460  GOSUB 1910
470  INPUT "ENTER RUN IDENTIFIER   ",I$
480  INPUT "COLLECTION TIME IS?     ",T1
490  INPUT "CALIBRATOR FLUSH TIME IS?    ",T2
500  INPUT "TRAP FLUSH TIME IS?    ",T4
510  INPUT "TRAP COOL DOWN TIME IS?",T5
520  IF F(4)<>1 THEN 540
530  INPUT "HOW MANY AMBIENT SAMPLES BETWEEN CALIBRATIONS?   ",F(3)
540  INPUT "PROGRAM TRACE?   (1=YES)    ",F(2)
550  IF F(2)=1 THEN 580
```

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```
560  PRGM ANNOTATION OFF
570  GOTO 590
580  PRGM ANNOTATION ON
590  F(1)=0
600  INPUT "LIST VALVES?  (1=YES)    ";F(1)
610  INPUT "DO YOU WISH TO SEE RUN PARAMETERS?   (Y/N)   ";A$
620  IF A$<>"Y" THEN 670
630  LIST
640  INPUT "ANY CHANGES?  (Y/N)  ";A$
650  IF A$<>"Y" THEN 670
660  GOSUB 1800
670  INPUT "DO YOU WISH TO SEE THE RUN TABLE?  (Y/N)   ";A$
680  IF A$<>"Y" THEN 730
690  LIST RUN TBL
700  INPUT "ANY CHANGES?  (Y/N)   ";A$
710  IF A$<>"Y" THEN 730
720  GOSUB 1800
730  IF F(7)=1 THEN 2180
740  GOSUB 3530
750  IF F(4)<>1 THEN 1110
760  GOSUB 2450
770  GOSUB 1280
780  GOSUB 1230
790  PAGE
800  PRINT "MULTIPOINT CALIBRATION ZERO GAS RUN"
810  GOSUB 1660
820  SAVE REPORT 1 DEVICE# 16
830  GOSUB 1360
840  GOSUB 1230
850  PAGE
860  PRINT "MULTIPOINT CALIBRATION DILUTION FACTOR ";D(2)
870  GOSUB 1660
880  SAVE REPORT 2 DEVICE# 16
890  GOSUB 1410
900  GOSUB 1230
910  PAGE
920  PRINT "MULTIPOINT CALIBRATION DILUTION FACTOR ";D(3)
930  GOSUB 1660
940  SAVE REPORT 3 DEVICE# 16
950  GOSUB 1470
960  GOSUB 1230
970  PAGE
980  PRINT "MULTIPOINT CALIBRATION DILUTION FACTOR ";D(4)
990  GOSUB 1660
1000 SAVE REPORT 4 DEVICE# 16
1010 GOSUB 1530
1020 GOSUB 1230
1030 PAGE
1040 PRINT "MULTIPOINT CALIBRATION DILUTION FACTOR ";D(5)
1050 GOSUB 1660
1060 SAVE REPORT 5 DEVICE# 16
1070 GET REPORT TBL 100 DEVICE# 16
1080 GOSUB 3600
1090 GOSUB 3080
1100 GET REPORT TBL 1 DEVICE# 16
1110 GOSUB 1590
```

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```
1120 GOSUB 1230
1130 FOR I=1 TO F(3)
1140 F(19)=F(19)+1
1150 PAGE
1160 PRINT "AMBIENT SAMPLE #";I;"FROM ";I$
1170 GOSUB 1660
1180 EXECUTE S1,"SAVE REPORT"&VAL$(F(19))&"DEVICE#16"
1190 NEXT I
1200 PRINT "TURNING ALL VALVES OFF"
1210 GOSUB 1860
1220 STOP
1230 REM ****************************************VALVE LISTER
1240 IF F(1)<>1 THEN 1260
1250 LIST VALVE
1260 RETURN
1270 GOSUB 1860
1280 REM ****************************************FLUSH
1290 VALVE 7 ON
1300 VALVE 8 OFF
1310 VALVE 9 ON
1320 VALVE 10 ON
1330 VALVE 11 ON
1340 WAIT T2
1350 RETURN
1360 REM ****************************************GAS 4
1370 VALVE 8 ON
1380 VALVE 12 ON
1390 WAIT T2
1400 RETURN
1410 REM ****************************************GAS 3
1420 VALVE 8 ON
1430 VALVE 12 OFF
1440 VALVE 4 ON
1450 WAIT T2
1460 RETURN
1470 REM ****************************************GAS 2
1480 VALVE 8 ON
1490 VALVE 4 OFF
1500 VALVE 3 ON
1510 WAIT T2
1520 RETURN
1530 REM ****************************************GAS 1
1540 VALVE 8 ON
1550 VALVE 3 OFF
1560 VALVE 2 ON
1570 WAIT T2
1580 RETURN
1590 REM ****************************************AMBIENT CONFIG.
1600 GOSUB 1860
1610 VALVE 9 ON
1620 VALVE 10 ON
1630 VALVE 11 ON
1640 WAIT T2
1650 RETURN
1660 REM ****************************************INJECTION SUB
```


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```
1670 VALVE 1 ON
1680 VALVE 5 OFF
1690 WAIT T4
1700 OVEN TEMP INITIAL VALUE -50
1710 VALVE 5 ON
1720 WAIT T5
1730 VALVE 1 OFF
1740 WAIT T1
1750 VALVE 8 OFF
1760 START VALVE 1 ON
1770 OVEN TEMP INITIAL VALUE 150
1780 RETURN
1790 END
1800 REM ****************************************PARAMETER CHANGE DELAY
1810 PRINT "MAKE CHANGES NOW"
1820 WAIT 0.5
1830 INPUT "DO YOU REQUIRE MORE TIME?   (Y/N)   ",A$
1840 IF A$="Y" THEN 1810
1850 RETURN
1860 REM ****************************************VALVE OFFER SUB
1870 FOR I=1 TO 12
1880 EXECUTE S1,"VALVE "&VAL$(I)&"OFF"
1890 NEXT I
1900 RETURN
1910 REM ****************************************SINGLE POINT SELECT
1920 INPUT "REPEAT SINGLE POINT HOW MANY TIMES?    ",F(6)
1930 IF F(6)>10 THEN 1950
1940 GOTO 1980
1950 F(6)=10
1960 PRINT "MAXIMUM OF TEN"
1970 PRINT "TEN HAS BEEN SELECTED"
1980 F(7)=1
1990 INPUT "WHICH POINT?...(LOW) 1 2 3 4 (HIGH)   ",F(5)
2000 IF F(5)=1 THEN 2060
2010 IF F(5)=2 THEN 2090
2020 IF F(5)=3 THEN 2120
2030 IF F(5)=4 THEN 2150
2040 PRINT "INVALID OPTION"
2050 GOTO 1990
2060 F(8)=2
2070 F(18)=D(5)
2080 RETURN
2090 F(8)=3
2100 F(18)=D(4)
2110 RETURN
2120 F(8)=4
2130 F(18)=D(3)
2140 RETURN
2150 F(8)=12
2160 F(18)=D(2)
2170 RETURN
2180 REM ****************************************SINGLE POINT RUN
2190 GOSUB 3530
2200 GOSUB 2450
2210 GOSUB 1280
```


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```
2220 PAGE
2230 PRINT "SINGLE POINT CALIBRATION ZERO GAS RUN"
2240 GOSUB 1660
2250 F(20)=0
2260 GOSUB 2610
2270 SAVE REPORT 1 DEVICE# 16
2280 FOR S2=2 TO(F(6)+1)
2290 VALVE 8 ON
2300 EXECUTE S1," VALVE "&VAL$(F(8))&"ON"
2310 WAIT T2
2320 GOSUB 1230
2330 PAGE
2340 PRINT "SINGLE PT. CALIB.   GAS#";F(5);"  DILUTION FACTOR ";F(18)
2350 S5=S2-1
2360 PRINT "RUN#";S5;"OF";F(6)
2370 GOSUB 1660
2380 F(20)=F(18)
2390 EXECUTE S1," SAVE REPORT "&VAL$(S2)&" DEVICE# 16"
2400 NEXT S2
2410 GOSUB 3600
2420 GOSUB 3080
2430 GOTO 1110
2440 END
2450 REM ****************************************SUM VAR INIT
2460 FOR J=1 TO 10
2470 FOR K=1 TO 20
2480 X(J,K)=0
2490 NEXT K
2500 NEXT J
2510 RETURN
2520 REM ****************************************LIN REG SUB
2530 F(19)=X(6,I)
2540 M=X(5,I)-(X(1,I)*X(3,I))/F(19)
2550 M=M/(X(2,I)-(X(1,I)↑2/F(19)))
2560 B=(X(3,I)/F(19))-(M*(X(1,I)/F(19)))
2570 R=(X(5,I)-((X(1,I)*X(3,I))/F(19)))↑2
2580 R=R/(X(2,I)-((X(1,I)↑2)/F(19)))
2590 R=R/(X(4,I)-((X(3,I)↑2)/F(19)))
2600 RETURN
2610 REM ****************************************PEAK FINDER
2620 FOR N=1 TO #PEAKS
2630 IF CAL#(N)>0 THEN 2650
2640 GOTO 2710
2650 I=CAL#(N)
2660 A=AREA(N)
2670 IF F(30)<>1 THEN 2700
2680 GOSUB 3920
2690 GOTO 2710
2700 GOSUB 2730
2710 NEXT N
2720 RETURN
2730 REM ****************************************SUMMER SUB
2740 A=A-X(7,I)
2750 X(3,I)=X(3,I)+(F(20)*C(I))
2760 X(4,I)=X(4,I)+((F(20)*C(I))↑2)
```


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```
2770 X(1,I)=X(1,I)+A
2780 X(2,I)=X(2,I)+(A↑2)
2790 X(5,I)=X(5,I)+(A*(F(20)*C(I)))
2800 X(6,I)=X(6,I)+1
2810 RETURN
2820 REM ****************************************FID SUB
2830 Z$="FLAME IONIZATION DETECTOR"
2840 FOR I=1 TO 16
2850 GOSUB 2520
2860 M(1,I)=M
2870 B(1,I)=B
2880 R(1,I)=R
2890 NEXT I
2900 RETURN
2910 REM ****************************************REPORTER SUB
2920 PAGE
2930 PRINT Z$
2940 PRINT "          FOR    Y=MX+B"
2950 FOR K=1 TO 3
2960 PRINT
2970 NEXT K
2980 PRINT "COMPOUND","SLOPE","OFFSET","R SQUARED";"(N)"
2990 FOR L=1 TO F(28)
3000 READ L$
3010 PRINT L$
3020 PRINT,M(F(27),L),B(F(27),L),R(F(27),L);"(";X(6,L);")"
3030 PRINT
3040 PRINT
3050 NEXT L
3060 PAGE
3070 RETURN
3080 REM ****************************************ECD SUB
3090 GET CALIB 2 DEVICE# 16
3100 IF F(7)=1 THEN 3130
3110 F(19)=5
3120 GOTO 3140
3130 F(19)=(F(6)+1)
3140 Z$="ELECTRON CAPTURE DETECTOR"
3150 RESTORE
3160 GOSUB 2450
3170 FOR J=1 TO 20
3180 READ C(J)
3190 NEXT J
3200 FOR K=1 TO 5
3210 READ D(K)
3220 NEXT K
3230 FOR K=1 TO 16
3240 READ L$
3250 NEXT K
3260 FOR S5=1 TO 8
3270 C(S5)=10000
3280 NEXT S5
3290 FOR S3=1 TO F(19)
3300 IF F(7)=1 THEN 3330
3310 F(20)=D(S3)
```


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```
3320 GOTO 3340
3330 F(20)=F(18)
3340 F(29)=S3+100
3350 EXECUTE S1," GET REPORT "&VAL$(F(29))&" DEVICE# 16"
3360 F(30)=S3
3370 GOSUB 2610
3380 NEXT S3
3390 FOR S3=1 TO 8
3400 X(6,S3)=X(6,S3)+1
3410 NEXT S3
3420 F(27)=2
3430 FOR I=1 TO 8
3440 GOSUB 2520
3450 M(2,I)=M
3460 B(2,I)=B
3470 R(2,I)=R
3480 NEXT I
3490 F(28)=8
3500 GOSUB 2910
3510 GET CALIB 1 DEVICE# 16
3520 RETURN
3530 REM ****************************************START ON TIME
3540 PRINT "IT IS NOW";CLOCK;"HOURS"
3550 INPUT "ENTER START TIME...(HHMM)   ",F(22)
3560 F(21)=CLOCK
3570 IF F(22)<>F(21) THEN 3560
3580 PRINT "STARTING RUN AT";CLOCK
3590 RETURN
3600 REM ****************************************FID TESTER
3610 GET CALIB 1 DEVICE# 16
3620 IF F(7)=1 THEN 3650
3630 F(19)=5
3640 GOTO 3660
3650 F(19)=(F(6)+1)
3660 RESTORE
3670 FOR X=1 TO 20
3680 READ C(X)
3690 NEXT X
3700 FOR X=1 TO 5
3710 READ D(X)
3720 NEXT X
3730 GOSUB 2450
3740 Z$="FLAME IONIZATION DETECTOR"
3750 FOR S3=1 TO F(19)
3760 IF F(7)=1 THEN 3790
3770 F(20)=D(S3)
3780 GOTO 3800
3790 F(20)=F(18)
3800 EXECUTE S1," GET REPORT "&VAL$(S3)&" DEVICE# 16"
3810 F(30)=S3
3820 GOSUB 2610
3830 NEXT S3
3840 FOR S3=1 TO 16
3850 X(6,S3)=X(6,S3)+1
3860 NEXT S3
```

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```
3870 GOSUB 2920
3880 F(28)=16
3890 F(27)=1
3900 GOSUB 2910
3910 RETURN
3920 REM ****************************************ZERO POINTER
3930 X(7,I)=A
3940 RETURN
```

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APPENDIX B

TABLE 1B. RAW AREA VALUES FOR CANISTER SAMPLES

Compound	Canister 1				Canister 2			
	Sameday	Day 2	Day 4	Day 7	Sameday	Day 2	Day 4	Day 7
Propane	2.72	2.83	2.73	2.76	2.76	2.74	2.68	2.77
Vinyl Chloride	1.71	1.84	1.86	1.79	1.96	1.91	1.76	2.11
Vinylidene Chloride	2.01	2.15	2.17	2.16	2.10	2.18	2.09	2.17
Trichlorotri-fluoroethane	1.91	2.03	2.01	2.03	1.94	1.91	1.92	1.95
Chloroform	1.89	2.00	1.97	1.93	1.95	2.01	1.99	1.98
1,2 Dichloroethane	1.83	1.85	1.83	1.88	1.90	1.88	1.86	1.87
Methyl Chloroform	1.91	1.95	1.98	1.94	1.97	1.95	1.95	1.98
Carbon Tetrachloride	2.02	2.06	2.12	2.06	2.02	1.95	2.06	1.97
Trichloroethylene	1.75	1.79	1.81	1.80	1.92	1.90	1.82	1.79
1,3 Dichloropropene (cis)	0.80	0.72	0.67	0.76	0.81	0.78	0.75	0.73
1,3 Dichloropropene (trans)	0.60[a]	0.55	0.56[a]	0.61	0.66	0.65	0.64	0.54
1,2 Dibromoethane	2.31[a]	1.28[a]	1.29[a]	1.27[a]	1.42	1.45	1.42	1.38
Tetrachloroethylene	1.56	1.59	1.54	1.62	1.64	1.65	1.68	1.65
Chlorobenzene	1.30	1.38	1.37	1.39	1.50	1.52	1.47	1.52
Benzyl Chloride	0.99	0.96	0.73	0.95	1.16	1.00	0.78	0.69
Hexachlorobutadiene	1.54	1.54	1.79	1.93	1.71	1.48	1.51	1.90

Compound	Canister 3				Canister 4			
	Sameday	Day 2	Day 4	Day 7	Sameday	Day 2	Day 4	Day 7
Propane	2.75	2.73	2.75	2.78	2.56	2.73	2.74	2.76
Vinyl Chloride	1.85	1.83	1.90	1.85	1.86	1.80	1.78	1.77
Vinylidene Chloride	2.09	2.16	2.16	2.16	2.03	2.14	2.16	2.15
Trichlorotri-fluoroethane	1.89	1.92	1.88	1.93	1.91	1.97	1.99	2.02
Chloroform	2.08	2.11	2.05	2.03	1.82	2.00	1.90	1.94
1,2 Dichloroethane	1.95	1.92	1.88	1.92	1.78	1.84	1.85	1.90
Methyl Chloroform	1.97	1.99	1.96	1.95	1.90	1.96	1.97	1.94
Carbon Tetrachloride	1.96	2.14	2.16	1.98	2.00	2.06	2.06	2.02
Trichloroethylene	1.83	1.87	1.88	1.86	1.73	1.80	1.79	1.79
1,3 Dichloropropene (cis)	0.87	0.81	0.80	0.77	0.78	0.74	0.70	0.75
1,3 Dichloropropene (trans)	****	0.67[a]	0.67[a]	0.67[a]	****	0.58[a]	0.60[a]	0.64[a]
1,2 Dibromoethane	1.45	1.44	1.41	1.45	1.27	1.25	1.25	1.29
Tetrachloroethylene	1.65	1.64	1.65	1.65	1.48	1.56	1.58	1.57
Chlorobenzene	1.52	1.52	1.50	1.51	1.32	1.38	1.35	1.38
Benzyl Chloride	1.07	0.96	0.81	0.89	1.02	0.87	0.74	0.75
Hexachlorobutadiene	1.13	1.07	1.03	1.16	1.23	1.34	1.30	1.26

(a) Data not used in the statistical analysis (considered as outliers).

TABLE 1B. (Continued)

Compound	Canister 5				Canister 6			
	Sameday	Day 2	Day 4	Day 7	Sameday	Day 2	Day 4	Day 7
Propane	2.74	2.85	2.80	2.79	2.86	2.63	2.71	2.79
Vinyl Chloride	1.83	1.89	1.76	1.85	1.82	1.87	1.79	1.91
Vinylidene Chloride	2.08	2.19	2.09	2.16	2.11	2.14	2.15	2.17
Trichlorotri-fluoroethane	1.95	2.04	1.93	1.94	1.94	1.97	1.97	2.01
Chloroform	1.98	2.09	2.00	2.01	1.86	1.95	1.98	1.91
1,2 Dichloroethane	1.93	1.95	1.92	1.92	1.82	1.90	1.86	1.80
Methyl Chloroform	1.96	1.99	1.95	1.98	1.88	1.99	1.94	1.94
Carbon Tetrachloride	2.04	2.00	2.04	2.02	2.01	1.97	2.13	1.97
Trichloroethylene	1.84[a]	1.61[a]	2.44[a]	1.86[a]	1.75	1.80	1.92	1.81
1,3 Dichloropropene (cis)	0.84	0.81	0.82	0.81	****	0.79[a]	0.74[a]	0.77[a]
1,3 Dichloropropene (trans)	0.69	0.75	0.72	0.71	0.62	0.61	0.59	0.64
1,2 Dibromoethane	1.44	1.46	1.44	1.52	1.28	1.29	1.28	1.31
Tetrachloroethylene	1.61	1.68	1.61	1.68	1.56	1.60	1.58	1.61
Chlorobenzene	1.49	1.51	1.50	1.54	1.28	1.35	1.35	1.36
Benzyl Chloride	1.06	0.97	0.91	0.95	0.88	0.88	0.77	0.73
Hexachlorobutadiene	3.93[a]	7.35[a]	7.92[a]	9.59[a]	0.94	1.03	1.08	1.01

Compound	Canister 7			
	Sameday	Day 2	Day 4	Day 7
Propane	2.70	2.77	2.68	2.79
Vinyl Chloride	1.80	1.82	1.81	1.98
Vinylidene Chloride	2.09	2.16	2.15	2.15
Trichlorotri-fluoroethane	1.96	1.94	1.97	1.99
Chloroform	1.94	1.91	2.01	1.92
1,2 Dichloroethane	1.78	1.86	1.84	1.83
Methyl Chloroform	1.92	1.94	1.98	1.93
Carbon Tetrachloride	2.01	2.13	2.06	1.99
Trichloroethylene	1.72	1.82	1.82	1.79
1,3 Dichloropropene (cis)	1.32[a]	0.80[a]	0.74[a]	0.75[a]
1,3 Dichloropropene (trans)	0.62	0.60	0.62	0.63
1,2 Dibromoethane	1.27	1.33	1.32	1.32
Tetrachloroethylene	1.55	1.59	1.61	1.64
Chlorobenzene	1.33	1.38	1.35	1.33
Benzyl Chloride	0.88	0.91	0.83	0.77
Hexachlorobutadiene	0.93	1.04	1.01	1.07

(a) Data not used in the statistical analysis (considered as outliers).